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In support of this claim, enclosed is a certified copy(ies) of said foreign application(s). Said prior foreign application(s) is referred to in the oath or declaration. Acknowledgment of receipt of the certified copy(ies) is requested.

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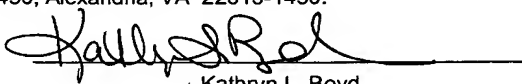

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Der Präsident des Europäischen Patentamts:
Im Auftrag

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Lithium transition metal phosphate powder for rechargeable batteries

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Lithium transition-metal phosphate powder for rechargeable batteries

The present invention relates to the field of lithium secondary batteries and especially to positive electrode materials operating at voltages greater than 3 V vs. Li^+/Li . The invention concerns the use of phosphates of transition metals as positive electrodes and allows the manufacturing of the olivine LiMPO_4 with controlled size and morphology, M being $\text{Fe}, \text{Co}, \text{Ni}, \text{Mn}_w$, with $0 \leq x \leq 1, 0 \leq y \leq 1, 0 \leq z \leq 1, 0 \leq w \leq 1$ and $x + y + z + w = 1$.

Lithium secondary batteries are now widely used in consumer electronics. They benefit from the light weight of lithium and from its strong reducing character, thus providing the highest energy density among known rechargeable battery systems. Lithium secondary batteries exist in various configurations depending on the nature of the electrode materials and of the electrolyte used. Commercialised Li-ion system use for instance LiCoO_2 and graphite respectively as positive and negative electrodes, with LiPF_6 in EC/DEC/PC as a liquid electrolyte. The operating voltage of the battery is related to the difference between thermodynamic free energies within the negative and positive electrodes. Solid oxidants are therefore required at the positive electrode, the materials of choice, up to now, being either the layered LiMO_2 oxides (M is Co or Ni) or the 3-dimensional spinel structure of LiMn_2O_4 . Extraction of lithium from each of these three oxides gives access to $\text{M}^{4+}/\text{M}^{3+}$ redox couples located between 4 and 5 V vs. Li^+/Li .

Three-dimensional structures using $(\text{XO}_4)^n$ polyanions instead of simple oxides have been proposed recently by J. B. Goodenough et al. in US-5,910,382 as viable alternatives to LiM_xO_y oxides. In particular, LiFePO_4 and $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ were said to be the most promising Fe-containing materials working at attractive potentials of 3.5 V and 2.8 V respectively vs. Li^+/Li . Both compounds operate with the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple and take advantage of the inductive effect of the XO_4^n groups that diminishes the strength of the Fe-O bond compared to a simple oxide.

Padhi et al. in J. Elec. Soc. 144(4) demonstrated the reversible extraction of lithium from olivine LiFePO_4 prepared at relatively high temperatures of 800 °C under Ar atmosphere from a solid/solid mixture of Li_2CO_3 or $\text{LiOH} \cdot \text{H}_2\text{O}$, $\text{Fe}(\text{CH}_3\text{COO})_2$ and $\text{NH}_4\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. The products used in the solid/solid reaction are costly, especially $\text{Fe}(\text{CH}_3\text{COO})_2$, and this process leads to LiFePO_4 particles of large average size, typically more than 30 μm . Only 60 to 70 %

of the theoretical capacity of 170 mAh/g was achieved at a very low charge/discharge rate of around C/80. Less capacity is to be expected at higher current densities of e.g. C/5.

5 Several authors reported improvements in the effective reversible capacity of LiFePO_4 . This was attained through various synthesis strategies that involved either the coating of electronic conductive carbon on LiFePO_4 particles (N. Ravet et al., Proc. Elec. Soc. Meeting, Hawai, 1999) or the use of strongly reactive Fe^{II} oxalate as a precursor for obtaining LiFePO_4 particles at moderate temperatures (Ri et al. in JP-2000-294238 or Yamada et al. in Elec. Soc. 148(3), A224 (2001)). The Fe^{II} oxalate precursor route described in JP-2000-294238 is a solid/solid
10 reaction that requires extensive grinding/mixing of the $\text{NH}_4\text{H}_2\text{PO}_4$, FeC_2O_4 and Li_2CO_3 precursors in acetone and evaporation under N_2 . This step is followed by a thermal treatment at temperatures ranging from 300 to 790 °C. The particle size obtained in this case was also around 30 μm .

15 In the prior art, Fe^{II} is selected as a starting product for the synthesis of LiFePO_4 . The synthesis is realised under inert (Ar or N_2) atmosphere so as to avoid the oxidation of Fe^{II} to Fe^{III} . However, Fe^{II} sources either are very expensive, e.g. Fe^{II} acetate, or may lead to the formation of strongly toxic gases, e.g. CO during the thermal decomposition of Fe^{II} oxalate. Moreover, these Fe^{II} precursors are prone to oxidation into Fe^{III} in air and must be handled under inert
20 atmosphere or under a non-aqueous solvent. Also, particle sizes of at least 30 μm were obtained and such coarse grain sizes lead to kinetic limitations, in particular when high charge/discharge rates are applied at ambient temperatures such as 25 °C.

Another problem in the effective use of LiFePO_4 as a positive electrode arises from its low
25 electronic conductivity and from the fact that both LiFePO_4 and FePO_4 are poor ionic conductors. Therefore, a certain amount of electronic conductive powder, such as Acetylene Black, has to be intermixed with the lithium transition-metal phosphate powder. In the case of JP-2000-294238, the LiFePO_4 /Acetylene Black ratio was 70/25. Such a high content of electrical conducting agent penalises the overall specific capacity of the composite positive
30 electrode.

It is an object of the present invention to overcome at least some of the disadvantages of the above mentioned processes and products. The present invention discloses a new synthesis technique based on the use of components that may be dissolved in water to yield, after
35 decomposition and annealing under inert or reducing atmosphere, LiMPO_4 of controlled particle size.

A process for the manufacture of a LiMPO_4 powder is disclosed, comprising the steps of

- providing an equimolar aqueous solution of Li^{1+} , M^{2+} and PO_4^{3-} prepared by dissolving components which are susceptible to coexist as solutes in an aqueous system and which, upon heating at a temperature below 500°C , decompose to form a pure homogeneous Li and M phosphate precursor,
- evaporating the water from the solution, thereby producing a solid mixture,
- decomposing the solid mixture at a temperature below 500°C to form a pure homogeneous Li and M phosphate precursor, and
- annealing the precursor at a temperature of less than 800°C , in an inert or reducing atmosphere, thereby forming a LiMPO_4 powder, whereby M^{2+} is one or more of Fe^{2+} , Co^{2+} , Ni^{2+} and Mn^{2+} , and M is $\text{Fe}_x\text{Co}_y\text{Ni}_z\text{Mn}_w$, with $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$, $0 \leq w \leq 1$ and $x + y + z + w = 1$. Preferentially, in the step of annealing the precursor, the annealing temperature is less than 600°C .

In another embodiment of the invention, a process is disclosed for the manufacture of a LiFePO_4 powder, comprising the steps of

- providing an equimolar aqueous solution of Li^{1+} , Fe^{3+} and PO_4^{3-} prepared by dissolving components which are susceptible to coexist as solutes in an aqueous system and which, upon heating at a temperature below 500°C , decompose to form a pure homogeneous Li and Fe phosphate precursor,
- evaporating the water from the solution, thereby producing a solid mixture,
- decomposing the solid mixture at a temperature below 500°C to form a pure homogeneous Li and Fe phosphate precursor, and
- annealing the precursor Li and Fe phosphate at a temperature of less than 800°C in a reducing atmosphere, thereby forming a LiFePO_4 powder.

Preferentially, in the step of annealing the precursor, the annealing temperature is less than 600°C .

In this embodiment the invention allows the use of cheap and abundant Fe^{III} starting products such as $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or any other iron nitrate, to produce LiFePO_4 . It should be appreciated that the reduction of Fe^{III} to Fe^{II} can be completed by a short annealing step at relatively low temperatures in a reducing atmosphere, thereby ensuring that only limited grain growth occurs. It is believed that the high reactivity of the solid mixture is due to the extreme homogeneity obtained by the process according to the invention. In the solid/solid reactions according to the

prior art however, it is difficult to start from Fe^{III} bearing products, because the reduction of Fe^{III} to Fe^{II} necessitates a lengthy annealing step at high temperature, resulting in coarse particles with poor electrochemical characteristics and possible reduction of Fe^{II} to Fe metal.

5 Nevertheless, it is also possible to realise the synthesis of LiFePO_4 by the solid/solid reaction at low temperatures, in the range of 350 to 600 °C, thereby obtaining relatively fine grains of less than 5 μm , by starting from very finely ground materials (less than 1 μm , preferably less than 500 nm) and sufficiently reactive Fe^{III} salts such as amorphous $\text{FePO}_4 \cdot n\text{H}_2\text{O}$, and by using a reducing atmosphere during the synthesis, to convert essentially all the Fe^{III} to Fe^{II} .

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The invention also concerns a powder for use in lithium insertion-type electrodes with formula LiMPO_4 having an average particle size of less than 1 μm , whereby M is $\text{Fe}_x\text{Co}_y\text{Ni}_z\text{Mn}_w$ with $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$, $0 \leq w \leq 1$ and $x + y + z + w = 1$. Such a product can be obtained by controlling the temperature of the annealing step of the decomposed solid mixture. The
15 small particle size allows achieving high reversible capacities at high current densities and at 25 °C, which were not previously observed.

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The invention further concerns a powder for use in lithium secondary batteries, having the formula LiFePO_4 , and characterised by a reversible electrode capacity of at least 65 % of the theoretical capacity, when used as an active component in a cathode which is cycled between 2.70 and 4.15 V vs. Li^+/Li at a discharge rate of C/5 at 25 °C.

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The invention further concerns a process for the manufacture of a lithium insertion-type electrode comprising the steps of

- providing a mixture of a lithium metal phosphate powder synthesised according to the invention, and a conductive carbon bearing powder, and
- milling this mixture during a period of time so as to optimise the reversible electrode capacity of the electrode comprising said mixture.

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In particular, the invention concerns the above lithium insertion-type electrode, whereby the lithium metal phosphate powder is LiFePO_4 , the conductive carbon powder is Acetylene Black or Carbon Super P, the mixing ratio of LiFePO_4 /carbon is between 75/25 and 85/15, and the milling time is between 15 and 25 minutes.

The present invention also provides a positive electrode material, LiMPO_4 (M is $\text{Fe}_x\text{Co}_y\text{Ni}_z\text{Mn}_w$, with $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$, $0 \leq w \leq 1$ and $x + y + z + w = 1$) for use in rechargeable battery systems comprising an electrolyte, a negative electrode and a separator between the two electrodes.

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The details of the invention are illustrated in Figures 1 to 11.

Figure 1 is the X-ray diffraction pattern of LiFePO_4 according to the invention.

Figure 2 shows a microphotograph of LiFePO_4 obtained by solid/solid reaction at 800°C according to prior art.

10 Figures 3 (a) to (d) shows microphotographs of LiFePO_4 according to the invention and annealed at 500 , 600 , 700 and 800°C respectively.

Figure 4 is the potential (V) vs. x (intercalation in Li_xFePO_4) behaviour of LiFePO_4 according to the invention, annealed at 500°C , mixed with Carbon Super P for 20 minutes and measured at C/5 and 25°C .

15 Figure 5 shows the influence of the milling time (min.) of LiFePO_4 powder according to the invention with Carbon Super P on the electrochemical capacity (mAh/g) of the obtained electrode material.

Figure 6 is a comparison of the potential (V) vs. x (intercalation in Li_xFePO_4) behaviour of LiFePO_4 obtained by solid/solid reaction at 800°C according to prior art, (A) without and (B) with further grinding.

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Figure 7 shows a microphotograph of the further ground powder used for obtaining the results shown in Figure 6 (B).

Figure 8 is the potential (V) vs. x (intercalation in Li_xFePO_4) behaviour of LiFePO_4 according to the invention, annealed at 500°C and measured at C/50 and 25°C .

25 Figure 9 is the potential (V) vs. x (intercalation in Li_xFePO_4) behaviour of LiFePO_4 according to the invention, annealed at 500°C and measured at C/5 and 55°C .

Figure 10 is the potential (V) vs. x (intercalation in Li_xFePO_4) behaviour of LiFePO_4 according to the invention, annealed at 500°C and measured at C/5 and 80°C .

Figure 11 shows the influence of the number of cycles (N) on an electrode containing LiFePO_4 powder according to the invention on the electrochemical charge (C+) and discharge (C-) capacity (mAh/g) of the obtained electrode material.

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For the preparation of LiFePO_4 , an aqueous solution of a 1 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is first slowly added under stirring in air to an equal quantity of a 1 M aqueous solution of LiH_2PO_4 at a pH

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between 3 and 4. In a second step, the water is slowly evaporated in a known way between 80 and 175 °C in air, to produce a very homogeneous precursor mixture containing Li, Fe and P in the stoichiometric proportions of LiFePO_4 . More concentrated solutions can be used successfully without penalty towards the purity of the powder produced. The homogeneous precursor that contains Fe^{III} is annealed for 5 to 15 hours in a N_2/H_2 reducing atmosphere with e.g. 10 % H_2 at a temperature of at least 500 °C to yield a pure crystalline LiFePO_4 phase. One or two intermediate grindings can be applied during annealing to allow complete reduction of the Fe^{III} into Fe^{II} . Small amounts of Fe^{III} , preferably not exceeding 5 mole %, can be tolerated in the final product.

The X-ray diffraction pattern of powder obtained according to above process and annealed at 500 °C is shown in Figure 1. The diffraction peaks are indexed in the orthorhombic space group Pmnb of the olivine LiFePO_4 with unit-cell parameters of $a = 6.004 \text{ \AA}$, $b = 10.326 \text{ \AA}$ and $c = 4.691 \text{ \AA}$.

Figure 2 shows the geometry of a particle of LiFePO_4 prior art powder obtained at 800 °C through solid state reaction of $\text{Fe}(\text{CH}_3\text{COO})_2$, Li_2CO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ under Ar. The powder is characterised by an average particles size of about 50 μm and by a specific surface of less than 0.5 m^2/g .

The LiFePO_4 powder obtained by the process of the invention as illustrated in the example above is characterised by a small average particle size of less than 1 μm and a specific surface of 2 to 3 m^2/g . Adjustment of the particle size and of the specific surface can be obtained by controlling the annealing temperature between 500 and 800 °C. The invention provides thus an easy way of producing LiFePO_4 particles of desired sizes and morphologies. As can be seen in Figure 3 (a) to (d), increasing the annealing temperature results in a progressive increase in particle size and consequently in a decrease of the specific surface. Table 1 summarises the results.

Annealing temperature (°C)	500	600	700	800
Average particle size (μm)	<1 μm	1 μm	5 μm	25 μm
Specific surface (m^2/g)	2.84	1.06	0.54	0.30

Table 1. Influence of the annealing temperature on particle size and specific surface area.

The LiFePO_4 powder may be used effectively as a positive electrode in an electrochemical cell. Prior to the cell realisation, an intimate mixture of LiFePO_4 together with conducting carbon, preferably Acetylene Black or Carbon Super P, is produced. To this end, LiFePO_4 and carbon are introduced in the commonly used weight ratio of 83/17 in a stainless steel vessel, preferably filled with Ar, and ball milled for an adequate time with a milling apparatus such as a SPEX-8000. The LiFePO_4 particles are hereby coated with conductive carbon. Adding a binder for cell operation is not mandatory. The electrochemical characteristics of LiFePO_4 prepared by the process according to the invention are evaluated in a Swagelok cell configuration with lithium metal pasted on a nickel foil as the negative electrode and LiPF_6 in EC/DMC as the electrolyte. The electrochemical characteristics of LiFePO_4 as a function of the charge/discharge rate and of the temperature were evaluated.

LiFePO_4 particles were produced at an annealing temperature of 500 °C according to the invention, and milled with Carbon Super P (available from MMM Carbon, Belgium) in a weight ratio of 83/17 for 20 minutes. The obtained powder behaves very well at a high charge/discharge rate of C/5, i.e. one lithium extracted or inserted within 5 hours: as can be seen in Figure 4, 67 % of the theoretical value of 170 mAh/g is observed, which equals to a reversible capacity of 114 mAh/g.

Figure 5 shows a graph with the relationship between milling time of LiFePO_4 particles with Carbon Super P and the reversible capacity obtained. It can be observed that the milling time has a considerable influence and that an optimum milling time can be established, e.g. in the range of between 15 and 25 minutes for the SPEX-8000 milling apparatus.

The positive electrode of the invention may be used in either Li-ion type batteries with carbon at the negative electrode and a non-aqueous liquid electrolyte, or, when operating at 80 °C, in polymer-type batteries with metallic lithium at the negative electrode and a POE-type polymer as the electrolyte. When M is Co, Ni or Mn, the use is restricted to non aqueous liquid electrolyte systems, providing that the electrolyte used is stable at the high operating voltage of more than 4 V of the cell.

As an illustration of the improvements achieved by the invention, the particles of a prior art LiFePO_4 powder as shown in Figure 2, i.e. obtained at 800 °C from a solid state reaction under Ar of $\text{Fe}(\text{CH}_3\text{COO})_2$, Li_2CO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$, were mixed with Carbon Super P in a weight

ratio of 83/17 and tested in an electrochemical cell built in the Swagelok configuration. The positive electrode composite was deposited directly on the aluminium current collector. The electrochemical response of the powder is given in Figure 6 (A). The characteristic voltage curves as a function of x in Li_xFePO_4 were obtained at equivalent charge/discharge rate of C/5 and 25 °C. As can be seen, during charge/discharge cycling only 40 % of the theoretical capacity is reached.

It is essential to realise that further grinding of the particles of a prior art LiFePO_4 powder does not lead to powders obtainable by the low-temperature synthesis of the invention which are characterised by small particles. Indeed, extensive grinding of the prior art LiFePO_4 particles did not result in efficient comminution. This can be seen by comparing Figure 2, showing a typical prior art LiFePO_4 particle before further grinding, and Figure 7, showing a typical prior art LiFePO_4 particle after 90 minutes of grinding and 15 minutes of milling with carbon using a SPEX-8000 milling apparatus.

Moreover, amorphisation of the powder, and thus loss of the electrochemical activity of the olivine LiFePO_4 , occurs during grinding: Figure 6 (B) indeed shows that the relative capacity degrades from 40 % before grinding to 15 % after grinding.

For the composite electrode prepared with LiFePO_4 synthesised according to the invention at an annealing temperature of 500 °C and mixed in a 83/17 weight ratio with Carbon Super P, the effects of the cycling regime and of the temperature on the observed charge and discharge behaviour are summarised in Figures 8 to 10. As can be seen in Figure 8, the slow kinetics of the front-type reaction between LiFePO_4 and FePO_4 are less penalising at a slower charge/discharge rate, as a reversible electrode capacity of 80 % of the theoretical capacity for a charge/discharge rate of C/50 is observed. Also, as illustrated in Figure 9 and 10, the kinetics improve with increasing operating temperature of the electrochemical cell. A reversible capacity as high as 90 % of the theoretical capacity is reached at 80 °C. Moreover, it is remarkable to observe the very small polarisation of the electrochemical cell under these conditions.

Finally, tests have shown the high stability of LiFePO_4 , even when cycled at a relatively high temperature of 55 °C, as is demonstrated in Figure 11. The cycling was performed at charge and discharge rates of C/10.

Claims

1. Process for the manufacture of a LiMPO_4 powder, comprising the steps of

- 5 - providing an equimolar aqueous solution of Li^{1+} , M^{2+} and PO_4^{3-} prepared by dissolving components which are susceptible to coexist as solutes in an aqueous system and which, upon heating at a temperature below 500°C , decompose to form a pure homogeneous Li and M phosphate precursor,
- evaporating the water from the solution, thereby producing a solid mixture,
- 10 - decomposing the solid mixture at a temperature below 500°C to form a pure homogeneous Li and M phosphate precursor, and
- annealing the precursor at a temperature of less than 800°C , in an inert or reducing atmosphere, thereby forming a LiMPO_4 powder, whereby M^{2+} is one or more of Fe^{2+} , Co^{2+} , Ni^{2+} and Mn^{2+} , and M is $\text{Fe}_x\text{Co}_y\text{Ni}_z\text{Mn}_w$, with $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$, $0 \leq w \leq 1$ and $x + y + z + w = 1$.
- 15

2. Process according to claim 1, whereby in the step of annealing the precursor, the annealing temperature is less than 600°C .

3. Process for the manufacture of a LiFePO_4 powder, comprising the steps of

- providing an equimolar aqueous solution of Li^{1+} , Fe^{3+} and PO_4^{3-} prepared by dissolving components which are susceptible to coexist as solutes in an aqueous system and which, upon heating at a temperature below 500°C , decompose to form a pure homogeneous Li and Fe phosphate precursor,
- 25 - evaporating the water from the solution, thereby producing a solid mixture,
- decomposing the solid mixture at a temperature below 500°C to form a pure homogeneous Li and Fe phosphate precursor, and
- annealing the precursor at a temperature of less than 800°C in a reducing atmosphere, thereby forming a LiFePO_4 powder.
- 30

4. Process according to claim 3, whereby in the step of annealing the precursor, the annealing temperature is less than 600°C .

5. Process according to claims 3 or 4, whereby the Fe^{3+} bearing component is iron nitrate.

6. A powder for use in lithium insertion-type electrodes with formula LiMPO_4 having an average particle size of less than $1\text{ }\mu\text{m}$, whereby M is $\text{Fe}_x\text{Co}_y\text{Ni}_z\text{Mn}_w$ with $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$, $0 \leq w \leq 1$ and $x + y + z + w = 1$.

5 7. A powder for use in lithium insertion-type electrodes, in particular according to claim 6, having the formula LiFePO_4 , and characterised by a reversible electrode capacity of at least 65 % of the theoretical capacity, when used as an active component in a cathode which is cycled between 2.70 and 4.15 V vs. Li^+/Li at a discharge rate of C/5 at 25 °C.

10 8. A powder for use in lithium insertion-type electrodes obtainable by a process according to claims 2 or 4.

9. A battery comprising a lithium insertion-type electrode, containing a powder according to claims 6 to 8.

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10. Process for the manufacture of a lithium insertion-type electrode comprising the steps of

- providing a mixture of a lithium metal phosphate powder according to claims 6 to 8 and a conductive carbon bearing powder, and
- milling this mixture during a period of time so as to optimise the reversible electrode

20 capacity of the electrode comprising said mixture.

11. Process according to claim 10, whereby the lithium metal phosphate powder is LiFePO_4 , the conductive carbon powder is either one of Acetylene Black and Carbon Super P, the weight ratio of LiFePO_4 /carbon is between 75/25 and 85/15, and the milling time is between

25 15 and 25 minutes.

Abstract

5 The invention concerns the manufacture and use of phosphates of transition metals as positive electrodes for secondary lithium batteries and discloses a process for the production of LiMPO_4 with controlled size and morphology, M being $\text{Fe}_x\text{Co}_y\text{Ni}_z\text{Mn}_w$, with $0 \leq x \leq 1$, $0 \leq y \leq 1$, $0 \leq z \leq 1$, $0 \leq w \leq 1$ and $x+y+z+w=1$.

10 A process is disclosed for the manufacture of LiFePO_4 , comprising the steps of

- providing an equimolar aqueous solution of Li^{1+} , Fe^{3+} and PO_4^{3-} ,
- evaporating the water from the solution, thereby producing a solid mixture,
- decomposing the solid mixture at a temperature below 500°C to form a pure homogeneous Li and Fe phosphate precursor, and
- annealing the precursor at a temperature of less than 800°C in a reducing atmosphere,

15 thereby forming a LiFePO_4 powder.

The obtained powders have a particle size of less than $1\text{ }\mu\text{m}$, and provide superior electrochemical performances once mixed for an appropriate time with electrical conductive powder.

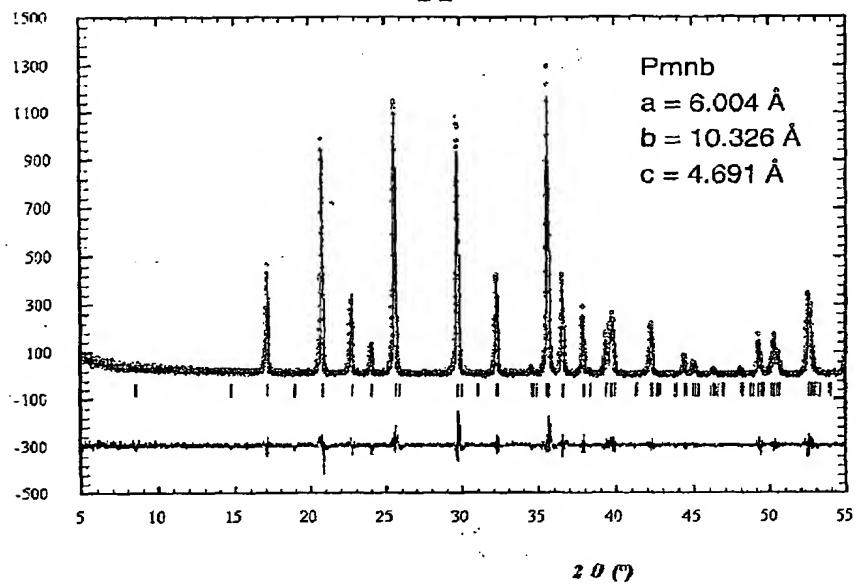


Fig. 1

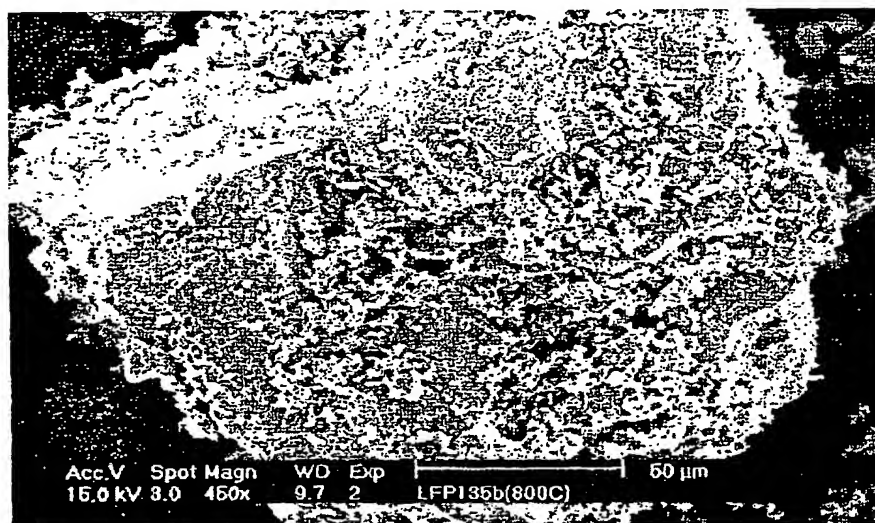


Fig. 2

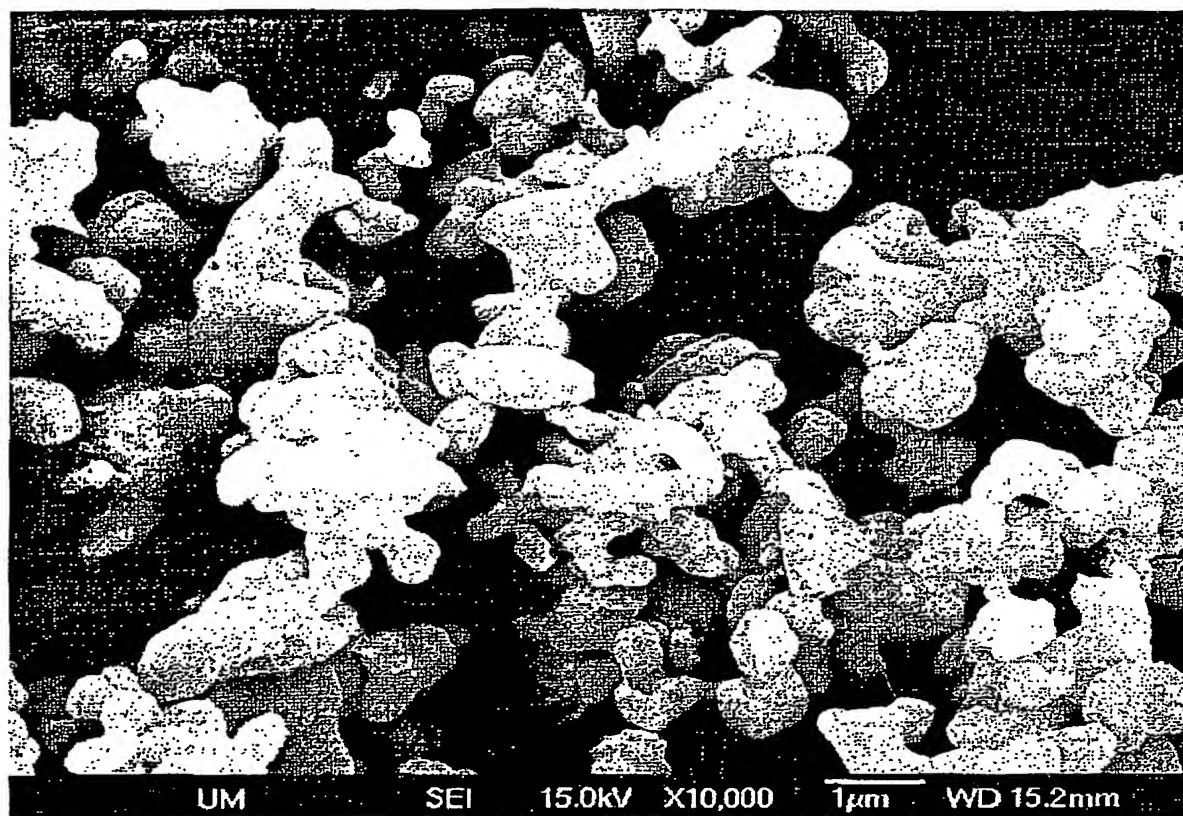


Fig. 3 (a)

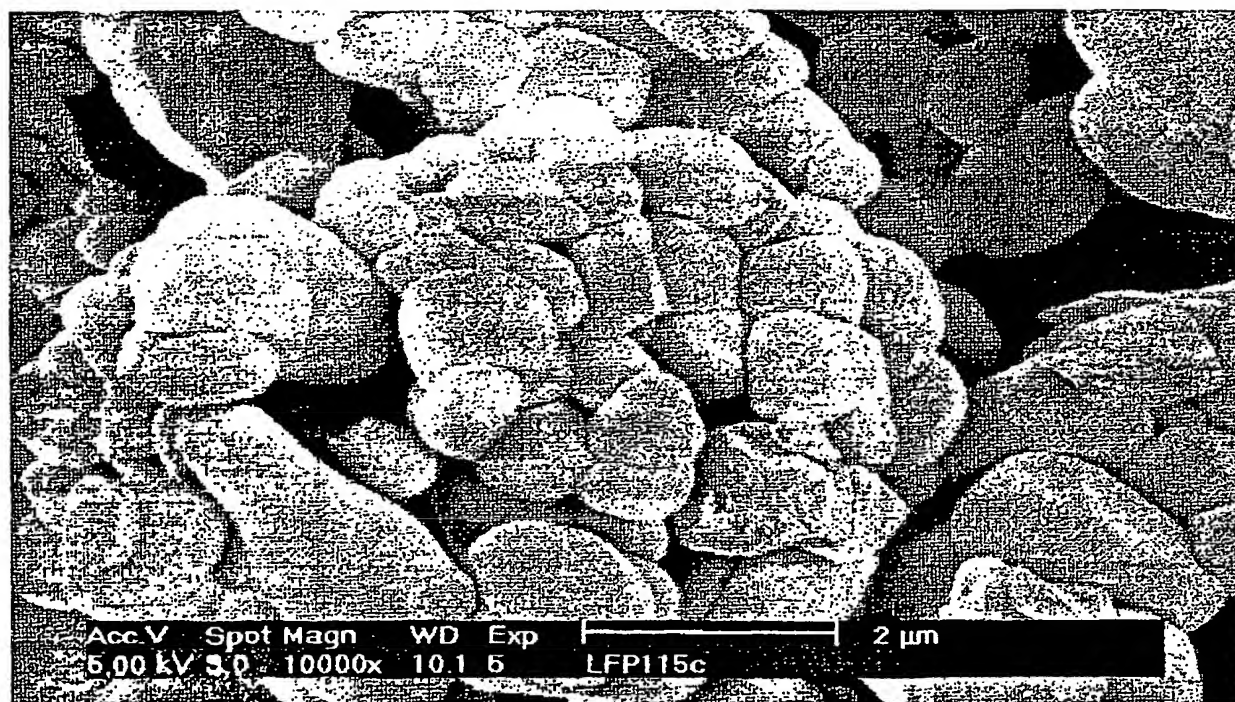


Fig. 3 (b)

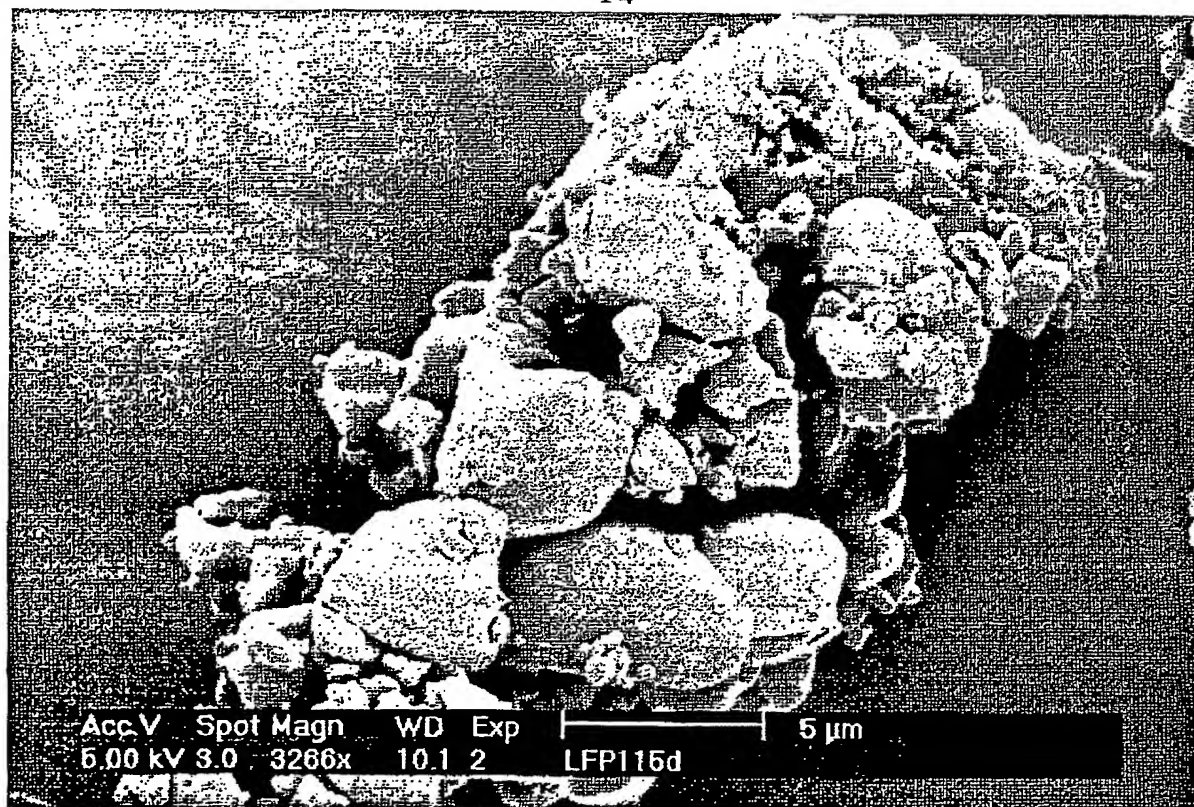


Fig. 3 (c)

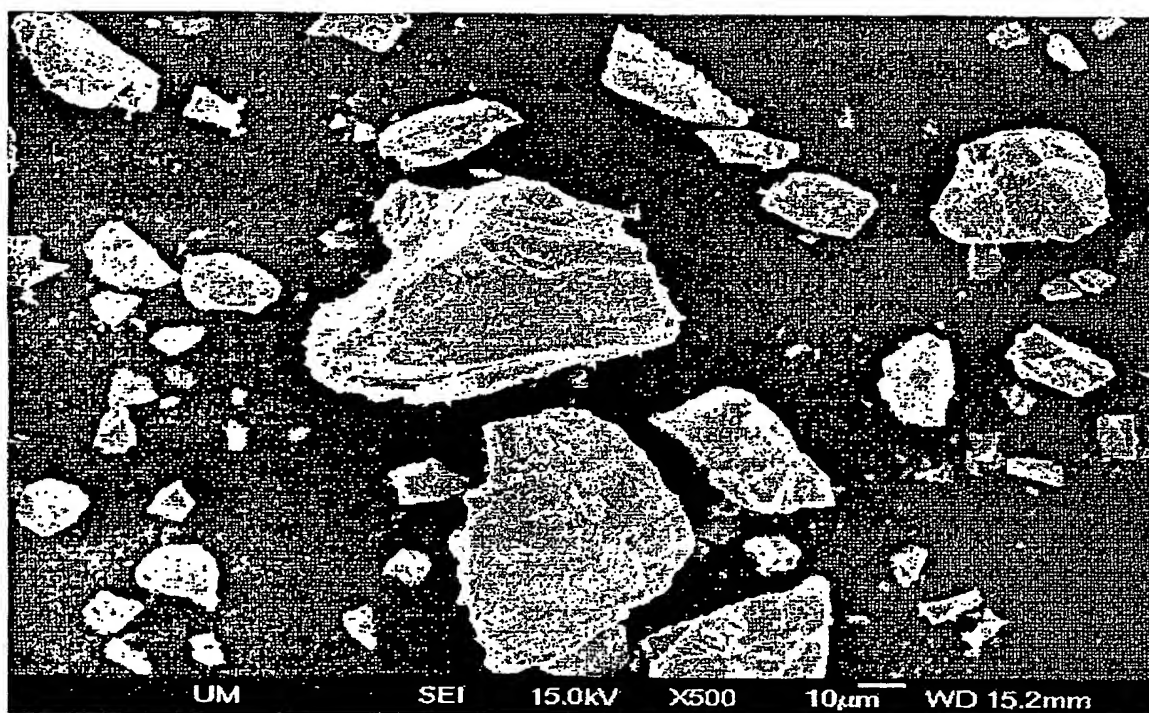


Fig. 3 (d)

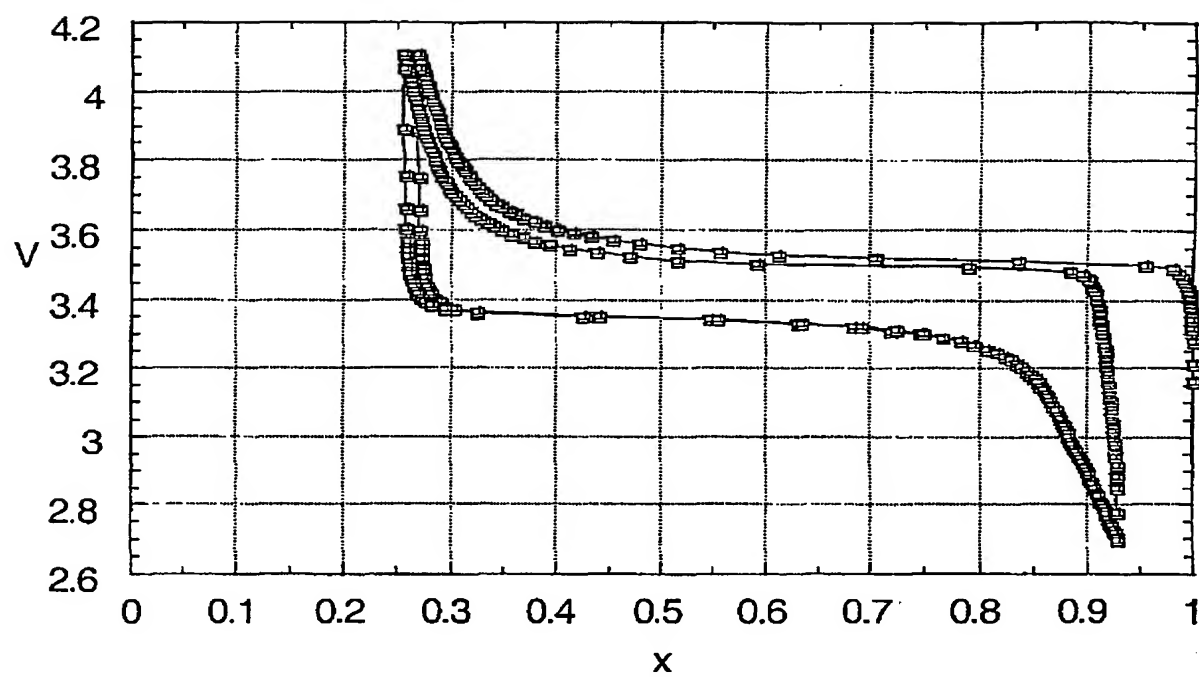


Fig. 4

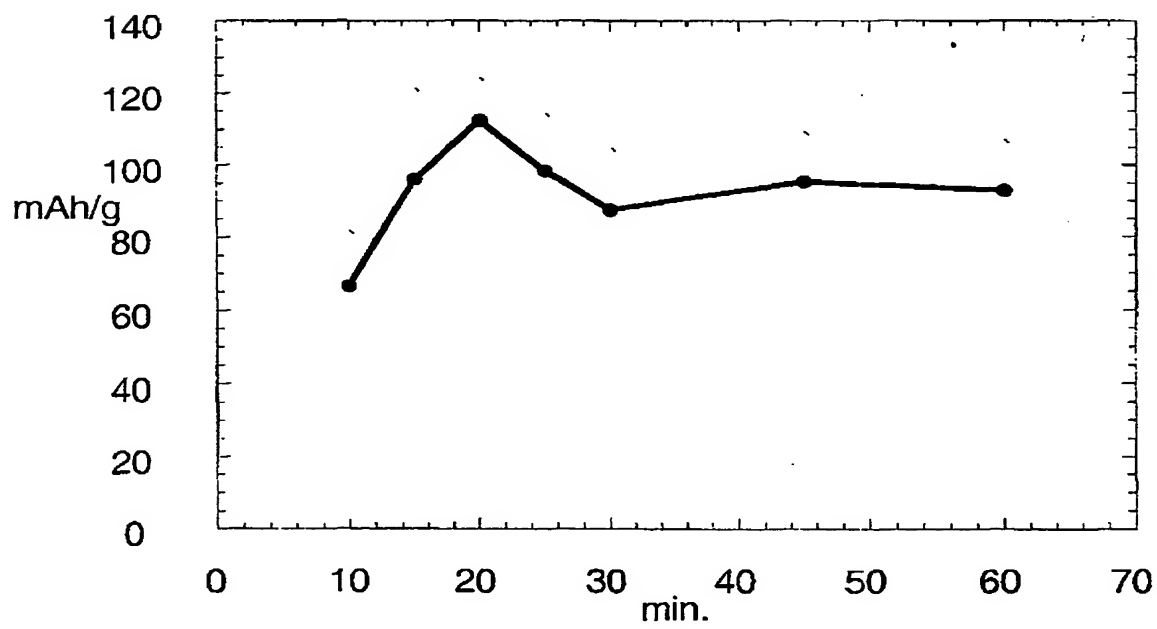


Fig. 5

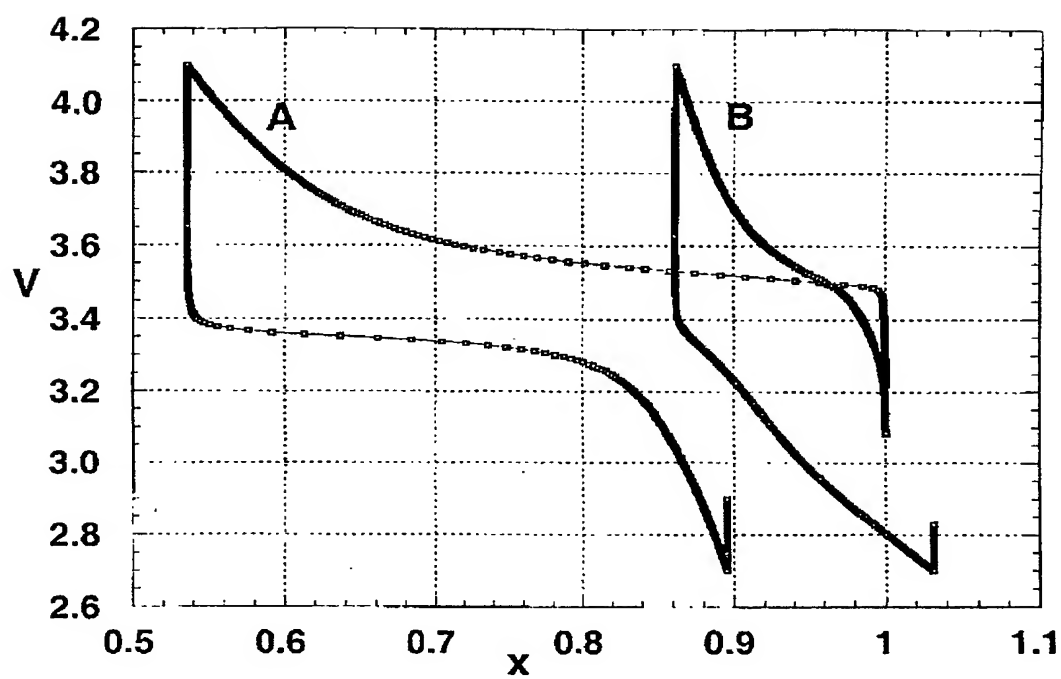


Fig. 6

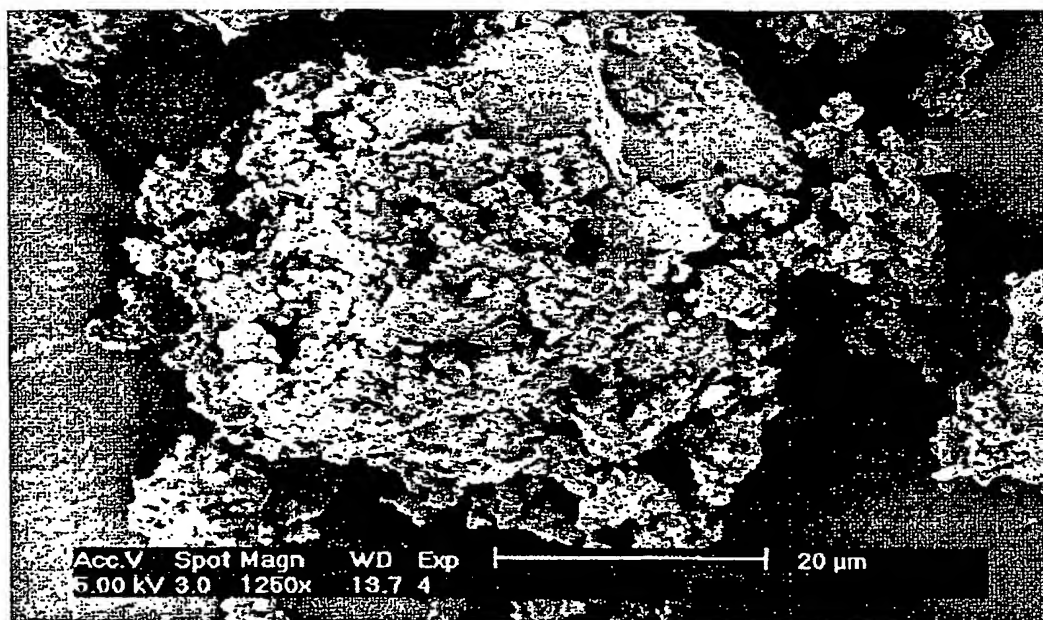


Fig. 7

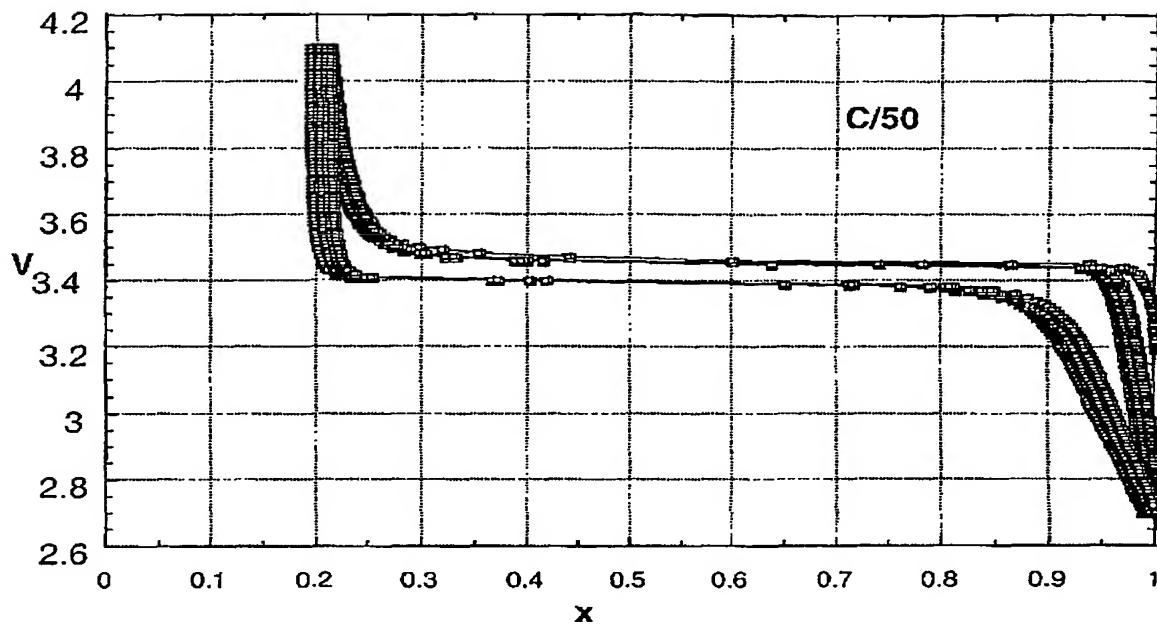


Fig. 8

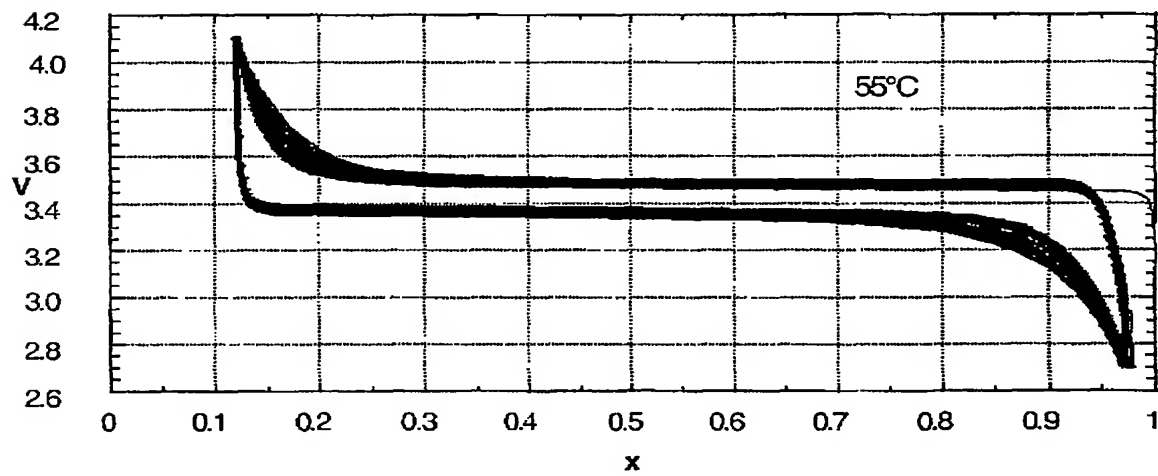


Fig. 9

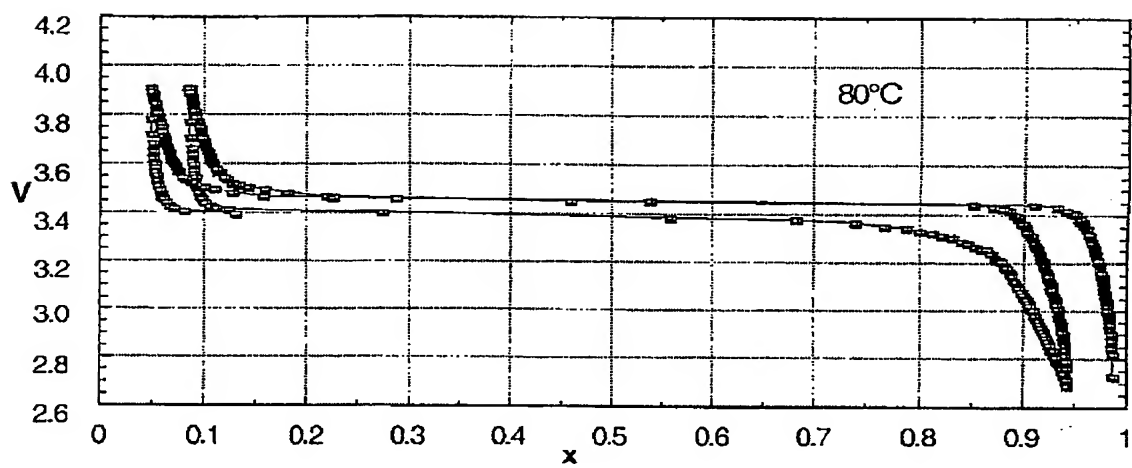


Fig. 10

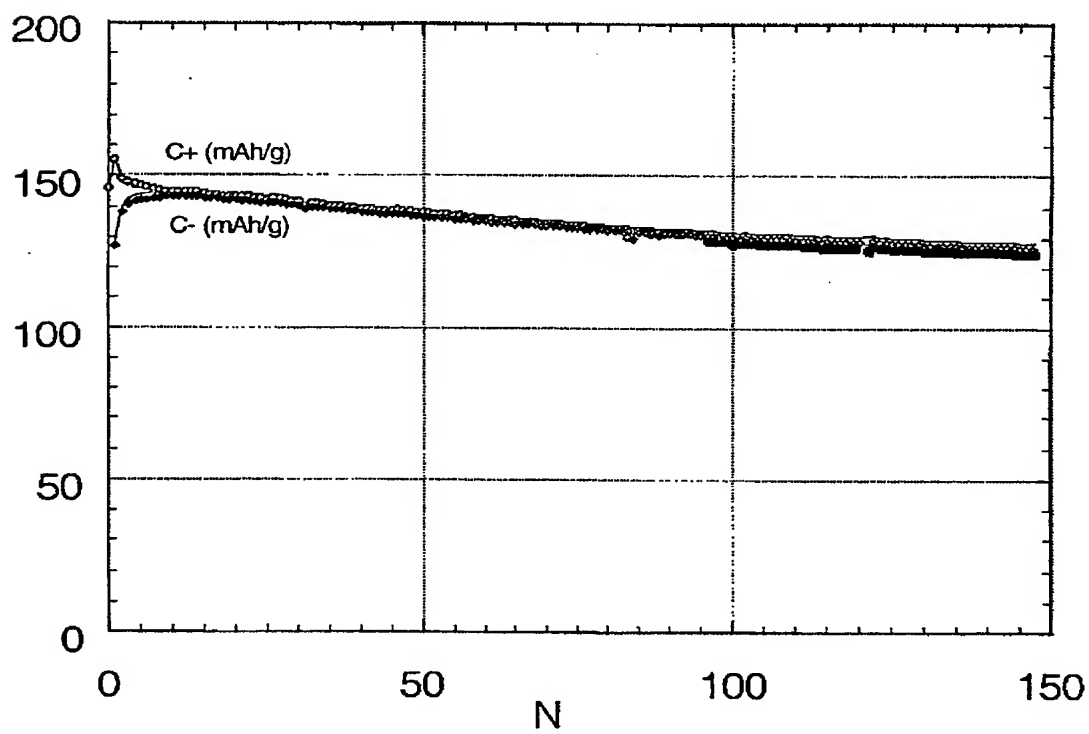


Fig. 11